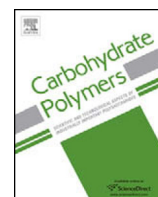




ELSEVIER

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Gelation of rhamnogalacturonan I is based on galactan side chain interaction and does not involve chemical modifications

Polina V. Mikshina^{a,*}, Olga N. Makshakova^a, Anna A. Petrova^a, Ilzira Z. Gaifullina^a, Bulat Z. Idiyatullin^a, Tatyana A. Gorshkova^a, Yuriy F. Zuev^{a,b}^a Kazan Institute of Biochemistry and Biophysics, Kazan Scientific Center, Russian Academy of Sciences, 420111, Lobachevsky Str., 2/31, Kazan, Russian Federation^b Kazan (Volga Region) Federal University, Kazan, 420008, Kremlevskaya Str., 18, Kazan, Russian Federation

ARTICLE INFO

Article history:

Received 1 March 2017

Received in revised form 24 April 2017

Accepted 4 May 2017

Available online 4 May 2017

Keywords:

rhamnogalacturonan I

galactan

microwave-induced gelation

NMR-spectroscopy

FTIR-spectroscopy

ABSTRACT

The article presents the structural principles of microwave-induced formation of new gel type from pectic rhamnogalacturonan I (RG-I). The backbone of gel-forming RG-I does not contain consecutive galacturonic residues and modifying groups that can be the cause of junction zone formation as it occurs in course of classical ways of pectin gelation. Microwave irradiation does not cause destruction and chemical modifications of RG-I. Removal of half of galactan chains from RG-I leads to loss of gelling capability pointing out on their leading role in this process. Rising of intensity of the bands attributed to galactose and glycosidic linkages in RG-I gel comparing to solution where this polymer exists as molecule associate indicates that the spatial organization of galactans in gel is changed. A model of the RG-I gelation is proposed: being destabilized at volumetric microwave heating RG-I associates are repacked forming network where RG-I molecules are entangled by galactan chains.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The ability to gelation is the well-known property of many matrix polysaccharides of land plant and algae cell walls. This property provides the survival of algae in conditions of constant wave exposure and drying, as well as the formation of the integrity of plant tissues and organs (Bochkov, Afanasiev, & Zaikov, 1980, Ch. 4; Daher & Braybrook, 2015; McCartney & Knox, 2002; Rees & Welsh, 1977). The ability to form gels is widely exploited in industry, food technology, medicine applications and cosmetology. Attractiveness of polysaccharides as ubiquitous, renewable, biodegradable and non-toxic resources for various applications gave rise to numerous research studies, the topics of which cover wide range of gel properties, such as working temperatures and pH, rheological properties, junction zone structure, etc. Alginates and sulfated galactans (agars and carrageenans) from algae and pectin from higher plants are among the most well-known gel-forming polysaccharides. The

presence of the negatively charged groups (sulfate or carboxyl) and/or various substituents (methyl, acetyl, etc.) as well as the absence of backbone substitution by side chains are the key structural features of these polysaccharides that provide the ability to interact and to form the junction zones at gelation (Thakur, Singh, Handa, & Rao, 1997).

Gelation of branched heteropolysaccharides is not quite typical. However, gel formation by plant ramified heteropolysaccharide – rhamnogalacturonan I (RG-I), rhamnosyl residues of which are substituted by neutral galactan side chains – has been described recently (Mikshina, Petrova, Idiyatullin, Zuev, & Gorshkova, 2015). This polysaccharide is obtained from cell wall of flax gelatinous fibers (Gurjanov, Ibragimova, Gnezdilov, & Gorshkova, 2008). Its backbone is built of repeating dimers [$\rightarrow 4$]- α -D-GalpA-($1 \rightarrow 2$)- α -L-Rhap($1 \rightarrow$); that defines the name and refers it to the pectins. The complexity of flax fiber RG-I structure is provided by the β -($1 \rightarrow 4$)-galactan side chains, which are attached to the O-4 of rhamnose and may have different lengths and minor components in the structure (Gurjanov et al., 2008; Mikshina et al., 2012). The average length of oligomeric side chain of flax cell wall RG-I is 14 galactose residues; a rare branching of the side chains by Araf or Galp linked by other than β -($1 \rightarrow 4$) types of linkages does not exceed 3–4% (Mikshina et al., 2012). In water solution, the RG-I possesses a peculiar spatial organization: it forms the self-associates with side chains located in

* Corresponding author.

E-mail addresses: p.mikshina@gmail.com (P.V. Mikshina), makshakova@gmail.com (O.N. Makshakova), anna.an.petrova@gmail.com (A.A. Petrova), gaifullina9292@mail.ru (I.Z. Gaifullina), cognizer@mail.ru (B.Z. Idiyatullin), gorshkova@kibb.knc.ru (T.A. Gorshkova), yufzuev@mail.ru (Y.F. Zuev).